

# NO<sub>x</sub> Formation in the Local Temperature of Natural Gas Fired Reheating Furnaces

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## 1.0 Introduction

The investigation of the NO<sub>x</sub> emissions of natural gas fired reheating furnaces is a special task which involves the investigation of the equilibrium relations of reactions producing NO<sub>x</sub> at the temperature of such furnaces, i.e. at a furnace hearth temperature of 900 to 1300 °C.

The first problem in investigating NO<sub>x</sub> emissions is to determine what role combustion and its reactions play in air pollution and what role NO<sub>x</sub> produced by the NO<sub>x</sub> producing materials released in dissociation and dissociation itself play. The research work was part of the OTKA 7451 Project sponsored by the Hung. Acad. of Sciences.

Before starting the investigation of the combustion reactions leading to NO<sub>x</sub> emissions, the task set was to study the role of dissociation at the temperature of industrial reheating and annealing furnaces. An answer was sought to the question of what amount of NO<sub>x</sub> the furnace gas is capable of producing during the time it stays in the chamber as a result of the furnace construction at the well defined chamber temperature and whether the time  $t$  has to be taken into account as a factor influencing NO<sub>x</sub> emissions of the furnaces.

Therefore thermodynamic and reaction kinetic calculations and experiments will be used to clarify whether a significant amount of NO (more than 1 ppm(V/V)) can be formed in flue gas or air at 1200 to 1700 K if there is no combustion taking place.

## 2. Reaction kinetic calculations

Nitrogen and oxygen can be combined in various compounds. These compounds have different stability at the same temperature and pressure. It can be established from analysing the thermodynamic data (1) of their formation that the equilibrium constants of the nitrogen oxide formation reactions increase with an increase in temperature, for the formation enthalpy of every oxide is a positive, i.e. endotherm process. It can also be stated that only the NO and NO<sub>2</sub> formations have to be significantly taken into account in the temperature interval of 1200 to 1700 K. In that temperature interval the equilibrium concentration of N<sub>2</sub>O, N<sub>2</sub>O<sub>3</sub>, N<sub>2</sub>O<sub>4</sub> and N<sub>2</sub>O<sub>5</sub> is so small that it can be neglected.

Table 1 gives the standard thermodynamic data (1) of nitrogen oxide formation which will later be used in the equilibrium and reaction kinetic calculations.

Table 1: Standard Thermodynamic Data of NO, N<sub>2</sub>O and NO<sub>2</sub> Formation

	1/2N <sub>2</sub> + 1/2O <sub>2</sub> = NO		N <sub>2</sub> + 1/2O <sub>2</sub> = N <sub>2</sub> O		1/2N <sub>2</sub> + O <sub>2</sub> = NO <sub>2</sub>	
	$\Delta H_T^\circ$ kJ	$\Delta G_T^\circ$ kJ	$\Delta H_T^\circ$ kJ	$\Delta G_T^\circ$ kJ	$\Delta H_T^\circ$ kJ	$\Delta G_T^\circ$ kJ
1200	90,52	75,27	84,37	171,05	32,24	108,51
1300	90,53	74,00	84,89	178,25	32,36	114,86
1400	90,55	72,72	84,41	185,41	32,49	121,19
1500	90,56	71,45	85,94	192,54	32,61	127,52
1600	90,56	70,18	86,47	199,63	32,77	133,85
1700	90,56	68,91	87,00	206,69	32,84	140,16
$\Delta G_T^\circ = 90,536 - 0,01272T$						

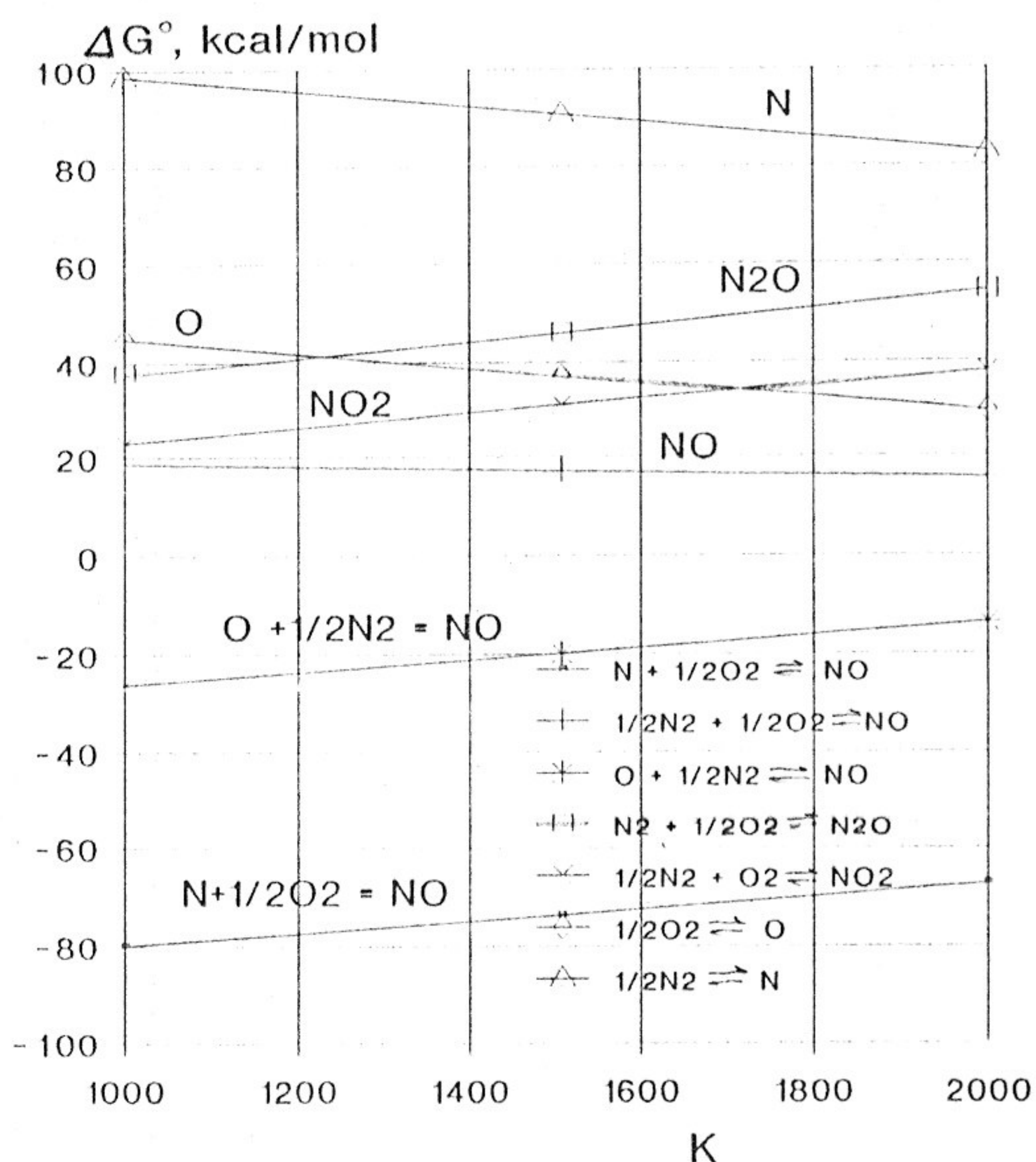


Fig. 1.

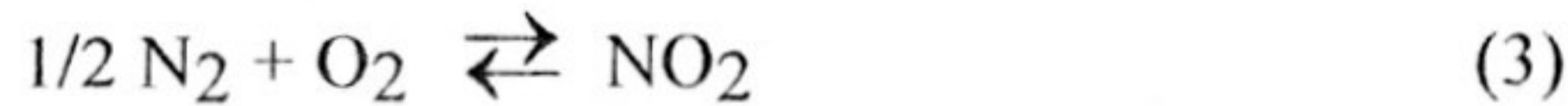
### 2.01 Equilibrium relations of NO, N<sub>2</sub>O and NO<sub>2</sub> formation

The formation of the above nitrogen oxides can be described by the following reaction equations:

Figure 1 shows the temperature dependency of the standard formation free enthalpies of the reactions. The diagram also shows the temperature dependency of the changes in the standard free enthalpy of the thermal dissociation of nitrogen and oxygen.

Before the reaction kinetic investigation of the formation and decomposition of nitrogen oxides, a survey of the equilibrium relations of their formation from air will be expedient.

The equilibrium concentration data obtained from these calculations will be the input data for the kinetic calculations on the one hand, and, on the other, will represent a theoretical limit value which can be used for controlling the data obtained by the kinetic calculation.



A reakciók egyensúlyi állandói a /bar-ban megadott/ parciális nyomásokkal kifejezve:

$$K_p^{/1/} = \frac{p_{\text{NO}}}{\sqrt{p_{\text{N}_2} p_{\text{O}_2}}}, \quad (4)$$

$$K_p^{/2/} = \frac{p_{\text{N}_2\text{O}}}{p_{\text{N}_2} \sqrt{p_{\text{O}_2}}}, \quad (5)$$

$$K_p^{/3/} = \frac{p_{\text{NO}_2}}{p_{\text{O}_2} \sqrt{p_{\text{N}_2}}}. \quad (6)$$

The equilibrium constants of the reactions as expressed in partial pressure (in bar) are as follows: (4), (5), (6)

Taking the partial pressures in air as initial values into consideration, the following expressions are obtained for the equilibrium partial pressures of the nitrogen oxides in Bar (For the sake of simplicity in solving the equations it is assumed that the extent of transformation in the reactions, i.e. the conversion is  $\ll 1$ . The relative error resulting from the simplification is only a small percentage in the temperature interval investigated):

$$p_{\text{NO}} = 0,41 K_p^{/1/}, \quad p_{\text{N}_2\text{O}} = 0,362 K_p^{/2/}, \quad p_{\text{NO}_2} = 0,187 K_p^{/3/} \quad (7)$$

As the gas reactions are homogeneous, various concentration units are found several times both in the equilibrium and in the kinetic calculations. Their conversion relationships for a pressure of 1 bar and temperature T in K are included in Table 2.

Table 2 : Conversion of the Units:

$$1 \text{ bar} = 100 \%(\text{V/V}) = 10^6 \text{ ppm}(\text{V/V}) = 1,242 \cdot 10^{-2} T^{-1} \text{ mol/cm}^3$$

$$1 \text{ ppm}(\text{V/V}) = 10^{-4} \%(\text{V/V}) = 1,242 \cdot 10^{-8} T^{-1} \text{ mol/cm}^3$$

$$1 \text{ mol/cm}^3 = 8,22 \cdot 10^3 T \%(\text{V/V}) = 8,22 \cdot 10^7 T \text{ ppm}(\text{V/V})$$

$$1 \%(\text{V/V}) = 1,242 \cdot 10^{-4} T^{-1} \text{ mol/cm}^3 = 10^4 \text{ ppm}(\text{V/V})$$

The formation free enthalpy data were used to calculate the equilibrium constants, which in turn were used to calculate the equilibrium partial pressure of the individual nitrogen oxides on the basis of the air composition and their concentration in various concentration units. As a result the following was obtained: the equilibrium concentration of  $\text{NO}_2$  changed in the range 1 to 10, and the concentration of  $\text{NO}$  changed in the range 200 to 3000 ppm(V/V) in the temperature interval 1200 to 1700 K. The equilibrium concentration of  $\text{N}_2\text{O}$  is negligible.

## 2.02 The dissociation equilibrium relations of oxygen and nitrogen

The reaction kinetic calculation required the determination of the thermal dissociation equilibrium relations of oxygen and nitrogen. From the thermodynamic data (1) (Table 3), the equilibrium partial pressures of the atomic state components were determined by the expressions:



From the equilibrium constants

$$K_{p4}^{\text{O}} = \frac{p_{\text{O}}}{\sqrt{p_{\text{O}_2}}} \quad K_{p5}^{\text{N}} = \frac{p_{\text{N}}}{\sqrt{p_{\text{N}_2}}} \quad (10)$$

of the dissociation reactions.

$$p_{\text{O}} = 0,46 K_p^{\text{O}} \quad p_{\text{N}} = 0,89 K_p^{\text{N}} \quad (11)$$

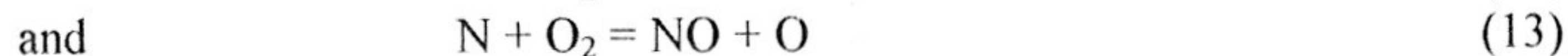
Table 3: Standard Thermodynamic Data of O<sub>2</sub> and N<sub>2</sub> Dissociation

	1/2N <sub>2</sub> ⇌ N		1/2O <sub>2</sub> ⇌ O	
	ΔH <sub>T</sub> <sup>0</sup> kJ	ΔG <sub>T</sub> <sup>0</sup> kJ	ΔH <sub>T</sub> <sup>0</sup> kJ	ΔG <sub>T</sub> <sup>0</sup> kJ
1200	477,57	399,26	253,50	174,71
1300	477,95	392,32	253,77	168,14
1400	478,31	386,17	254,04	161,56
1500	478,65	379,60	254,31	154,95
1600	478,98	372,99	254,56	148,34
1700	478,30	366,38	254,80	141,69

From the data in the Table it can be stated that the dissociation equilibrium constant of oxygen at standard pressure in air in the temperature interval investigated is 6 to 10 orders higher than that of nitrogen in air and under similar conditions. It results in the concentration of atomic nitrogen at the same temperature being negligible as compared to the concentration of atomic oxygen.

### 2.03 The speed of NO formation

In homogeneous gas reactions there is only little probability that new molecules are formed directly through the collision of gas molecules in simple reactions. The formation of NO from air should also be interpreted as a complex reaction with chain reactions. On the basis of the thermal dissociation relations of N<sub>2</sub> and O<sub>2</sub>, at the same temperature the probability of the formation of atoms O is significantly higher than that of atoms N, therefore NO is formed probably with a speed corresponding to the speed relations of the following two series(?) simultaneous reactions (2):



The speed of NO formation is:  $v_{\text{NO}} = \frac{d[\text{NO}]}{dt} = 2k[\text{O}][\text{N}_2]$  (14)

In air the nitrogen concentration is constant and it can be assumed that the thermal dissociation of oxygen is a relatively rapid process as compared to the speed of NO formation, therefore the instantaneous concentration of atomic oxygen does not depend either on NO concentration or on time, i.e. it is also constant. According to (8) the speed of NO formation is constant at a given temperature, i.e. NO concentration increases linearly with time.

In order to be able to determine the change in concentration with time, speed constant  $k$  and the instantaneous  $\text{N}_2$  and  $\text{O}$  concentration have to be known.

Speed constant  $k = 7 \cdot 10^{13} e^{-317000/8,314T}$  (15),

$\text{N}_2$  concentration in air is:  $c_{\text{N}_2} = 79\% \text{ (V/V)}$  ;

Assuming that the thermal dissociation of oxygen is a relatively rapid process, its instantaneous concentration can be taken into account with the same value as that of the equilibrium concentration under the same conditions, therefore for the equilibrium concentration of  $\text{O}$  for  $\text{O}_2\%(\text{V/V})$

$$c_{\text{O}} = K_{\text{p4}}^{\text{O}} [\text{O}_2]^{1/2} = 4,1 e^{-244\,800/8,314T} \sqrt{\text{O}_2\%(\text{V/V}) \frac{0,0001242}{T}}, \text{ mol/cm}^3. \quad (16)$$

After substituting the data, the following expression:

$$c_{\text{NO}} = 5,03 \cdot 10^{18} \sqrt{\frac{20,95}{T}} \exp\left\{-\frac{67576}{T}\right\} t, \text{ ppm} \quad (17)$$

is obtained for the time and temperature dependency of NO concentration in air.

Evaluating the calculated data it can be concluded that taking the order of 1 s reaction time (time in the chamber) as a basis, 1700 K is the temperature above which the speed of NO formation can become so great that an NO concentration of the order of ppm can develop without a combustion process for air composition conditions. NO concentration can increase as a function of time in the chamber so as to reach a value corresponding to equilibrium relation of equation (1).

The equilibrium NO concentration calculated at temperature 1700 K is appr. 3000 ppm, which can be reached in a time in the chamber of appr. 17 min. At the same time the calculated data show that as a result of the exponential temperature dependency at 2000 K, a time in the chamber of the order of seconds can be sufficient for an NO concentration of several ppm to develop in air and a few seconds for appr. 8000 ppm corresponding to equilibrium to develop.

## 2.04 The speed of NO decomposition

The ratio of the speed constants of the partial processes (the reactions in the directions of the top and bottom arrows) of homogeneous gas reactions equals the equilibrium constant of the gross reaction.

If the process of NO decomposition is assumed to be the process in the direction of the bottom arrow of reaction equation (6), then the equilibrium constant of that equation can be used to calculate the reaction speed constant of the decomposition. Table 4 contains the thermodynamic data of reaction (6).

Table 4 : Thermodynamic Data of Reaction (6)

	$\text{O} + \text{N}_2 \rightleftharpoons \text{NO} + \text{N}$	
$T$ K	$\Delta G_r^0$ kJ	$\ln K = - \Delta G_r^0 / RT$
1200	299,95	- 30,06
1300	298,66	- 27,63
1400	297,42	- 25,55
1500	296,17	- 23,75
1600	294,93	- 22,17
1700	293,67	- 20,78
$\Delta G_r^0 = 314,81 - 0,01245T$		

Using the equilibrium constant obtained from the thermodynamic data, relation

$$\frac{\overset{\leftarrow}{k}}{k} = \frac{\overset{\rightarrow}{k}}{K_6}$$

was used to determine the temperature function of speed constant:

$$K_6 = e^{-37864/T+1,5} \quad \overset{\rightarrow}{k} = 7 \cdot 10^{13} e^{-38128/T}, \text{ cm}^3/\text{mol.s}, \quad (17)$$

$$\text{and the temperature function is: } \overset{\leftarrow}{k} = 7 \cdot 10^{13} e^{-264/T-1,5}, \text{ cm}^3/\text{mol.s}. \quad (18)$$

The relation shows that the speed constant of NO decomposition practically hardly depends on temperature and in the temperature interval 1000 to 2000 K can be taken into account with a good approximation with constant

$$k = 1,25 \cdot 10^{13}, \quad \text{cm}^3/\text{mol.s} \quad (19)$$

The speed of NO decomposition can be given by the differential equation

$$d = -k \cdot c_{\text{NO}} \cdot c_{\text{N}} dt,$$

.. It can be assumed that the concentration of atomic nitrogen does not depend either on time, or on NO concentration, and its value is equal to the equilibrium concentration at the given temperature. For that assumption the differential equation is solved as follows

$$c_{\text{NO}}/c_{\text{NO}}^0 = e^{-k \cdot c_{\text{N}} \cdot t} \quad (20)$$

If the values  $k = 1,25 \cdot 10^{13} \text{ cm}^3/\text{mol} \cdot \text{s}$ , és  $c_{\text{N}}^{\text{kegyenes}} \text{ mol}/\text{cm}^3$  are substituted into the expression for the given temperature, then exponentially decreasing time functions will be obtained for the ratio  $c_{\text{N}}/c_{\text{NO}}^0$  at different temperatures.

The calculation results show that the NO decomposition process greatly slows down at a temperature below 1400 K. i.e. the process freezes. At the same time the half period of the decomposition speed decreases to a few seconds above 1700 to 1800 K.

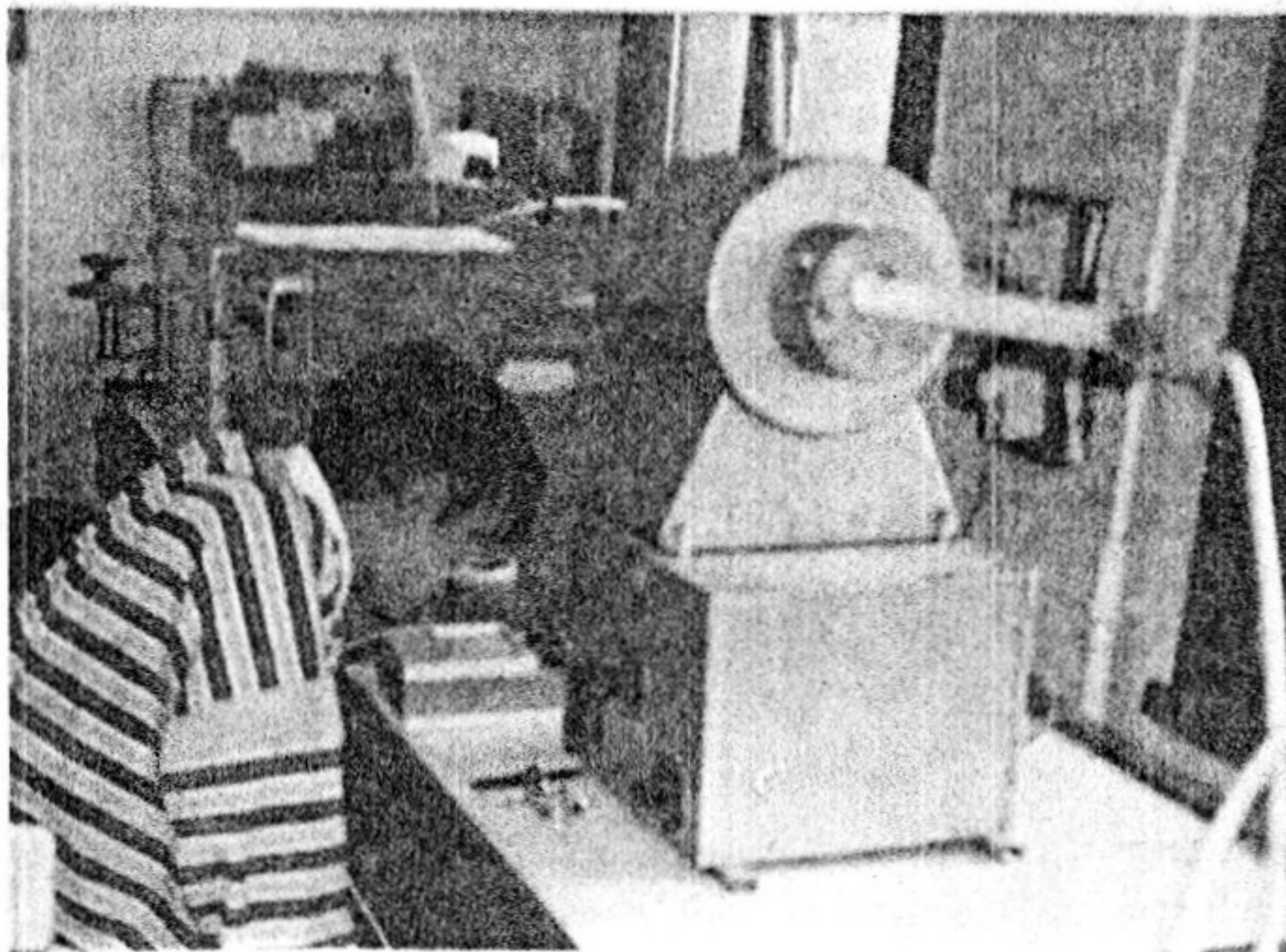
The investigation was performed in the framework of research project OTKA T-7451. The detailed calculations are included in the final report of the project (Annex 2).

### 3.0 Control by experiments

In order to control NO<sub>x</sub> formation without combustion, experiments were carried out at temperatures 1250 to 1400 °C with

- a/ 100% air
- b/ a mixture of 90% N<sub>2</sub> and 10% air
- c/ 100% flue gas

a/ Air was induced from the atmosphere through a pipe into an electric (MARS) furnace (Fig. 2). The ceramic pipe was 430 mm long, had an internal diameter of 19.5 mm and could be closed with a pin at both ends. The furnace was heated to the experimental temperature prior to the experiment.



A thermocouple, wrapped in a KAOWOOL paper cylinder, was introduced to the middle of the ceramic pipe to register temperature. The volume of the gas to be investigated was measured with a rotary meter in continuous flow, and for longer times in the chamber it was fed from a Dewille bottle.

Fig.2.

A longer and a shorter sampling tube were built into the ceramic pipe of the furnace. The shorter tube could be easily replaced by a cooled probe in order to cool the sample rapidly.

Before air was introduced, it was led through CaCl<sub>2</sub>, strong sulphuric acid and soda lime in order to dry it. For times of 20 to 240 min, the gas in the pipe was stored by closing the valves at the ends of the ceramic pipe.

The nitrogen - air mixture was mixed in a Dewille bottle of 10..50 dm<sup>3</sup> volume and was flowed from there through the furnace at a speed of e.g. 25 l/min.

The flue gas obtained from the combustion of the natural gas was produced in a cylindrical furnace and collected in a Dewille bottle. Before it was introduced into the MARS furnace, its NO<sub>x</sub> and O<sub>2</sub> contents were analysed.

The holding times were 1, 2, 4, 5, 6, 8, 10, 15, 20 and 60 minutes. Some experiments were conducted with longer times.

The measurements established how much the NO concentration increased in the flowing gas. At the end of the measurements the gas remaining in the Dewille bottle was analysed in order to register the possible NO decrease. It was established that the greatest decrease was from 87 to 84 ppmv. The results of the experiments with air are shown in the following table.

Temperature	Time, (min)				
°C.	2	10	20	30	60
1290	15				
1305		53			462
1310				202	
1320		70			511
1325		78			
1332		97			
1335					476
1340		110			
1345					518
1375			372		1389
1390		534			
1415		550	1071		
1420		615			

#### 4. Summary

The calculations and measurements proved that at the temperatures of 900 to 1300 °C of reheating furnaces after the completion of combustion no NO<sub>x</sub> increase greater than 1 ppmv took place in chamber time 1 to 10 sec customary in such furnaces.

#### Literature:

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Second Ed. Dept. of Commerce, USA, 1971.
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